

Low Platinum Loading Catalysts for Fuel Cells

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Objectives

- Further improve the new catalyst consisting of a submonolayer of Pt on carbon-supported Ru nanoparticles (1%Pt/10%Ru/C) to come close to the DOE's 2010 target of 100 $\mu\text{g}/\text{cm}^2$ noble metal loading.
- Further elucidate the inhibition mechanism of CO on H₂ oxidation on Pt.
- Reduce Ru loadings in Pt-Ru electrocatalysts.
- Explore monolayer-level-supported Pt electrocatalysts for O₂ reduction.

Technical Barriers

This project addresses the following technical barrier from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- Q. Electrode Performance

Approach

- Synthesize and characterize the electrocatalyst having a submonolayer of Pt on Ru nanoparticles and determine its CO tolerance.
- Test the new electrocatalyst in a membrane electrode assembly (MEA) at the Los Alamos National Laboratory.
- Use an in situ surface x-ray diffraction technique to follow the adsorption of CO on Pt during H₂ oxidation.
- Synthesize and test a non-noble metal alloy and early transition metal nanoparticles as support for Pt to reduce Ru loading.
- Prepare Pt monolayer/multilayer deposits on Au (111) and Au nanoparticles using our new method for depositing Pt monolayers and test these surfaces as O₂ reduction electrocatalysts.

Accomplishments

- The CO tolerance of the 1%Pt /10%Ru/C catalyst for oxidizing H₂ containing 1000 ppm CO at 2500 rpm was more than doubled compared with the last year's value. MEA stability tests at Los Alamos National Laboratory, conducted by Francisco Uribe and coworkers, showed a small loss in activity after 1000 hours of operation with combined H₂ and H₂ + 50 ppm CO + 4% air-bleed fuels. This catalyst has 1/10th (17 $\mu\text{g}/\text{cm}^2$) of the Pt loading of standard catalysts. For Pt, the loading of the new catalyst is below the DOE's target (150 $\mu\text{g}/\text{cm}^2$) for precious metals for 2004. For Ru, it is at the present level of state-of-the-art catalysts.

- The $(\sqrt{19} \times \sqrt{19})13\text{CO}$ phase was determined for the first time by x-ray diffraction technique on Pt(111): a fast $(2 \times 2) \leftrightarrow (\sqrt{19} \times \sqrt{19})$ phase transition was found. The oxidation of H_2 with 2% CO is inhibited by the formation of an ordered CO (2×2) adlayer.
- Pt on C-supported Au nanoparticles can be an efficient catalyst for reducing O_2 . A Pt mass specific activity 2.5 times higher than that of Pt10%/C was achieved. Its stability needs to be investigated.
- Pt on C-supported W nanoparticles may be a promising catalyst for H_2 oxidation.

Future Directions

- Optimize a Pt/Ru electrocatalyst, and conduct final tests at LANL and industrial laboratories.
- Investigate the possibilities of reducing Ru loading by non-noble metals, such as W.
- Explore Au-non-noble metal alloy nanoparticles as supports for a Pt monolayer for O_2 reduction.
- Investigate several low d-band vacancy metals as support for a Pt monolayer for O_2 reduction.

Introduction

We investigated a new catalyst consisting of a submonolayer of Pt on carbon-supported Ru nanoparticles (1%Pt/10%Ru/C) with the goal of improving its properties and further understanding the origins of its activity. Its catalytic activity was determined using a rotating thin-film disk electrode. The long-term stability and CO tolerance of this catalyst was tested in a fuel cell electrode (membrane electrode assembly) at Los Alamos National Laboratory. Several preliminary experiments were aimed at reducing the Ru loading. We also obtained new insights into the mechanism of poisoning the catalytic activity of a Pt(111) surface by CO.

The possibility of making an active catalyst for O_2 reduction consisting of Pt monolayers on metal nanoparticles on carbon support was explored. The initial results for Pt on Au indicate that very active catalysts can be obtained by this approach.

Approach

A new method for preparing Pt/Ru catalysts involving spontaneous deposition of Pt on Ru nanoparticles was further studied with the goal of optimizing it to increase the activity of the catalysts. In contrast to the Pt-Ru alloys catalysts, all the Pt atoms in this new one are available for the catalytic reaction. Therefore, the interaction of the Pt atoms with Ru, and the state of the Ru surface, are of utmost importance for the catalyst's activity. Ru-Ni and Ru-Co nanoparticles were deposited on carbon

using an impregnation method, while a Pt submonolayer was deposited on these nanoparticles spontaneously. The activity for H_2 oxidation and the CO tolerance were determined. The tests also were conducted with Pt clusters obtained by electroless deposition on polycrystalline W and carbon-supported W nanoparticles. Tungsten nanoparticles were obtained using BNL's new method of sonication solvolysis of W salts.

We employed an in situ x-ray diffraction technique using synchrotron radiation to follow the formation of ordered CO adlayers on Pt(111) during H_2 oxidation, monitoring the process as a function of time. The inhibition of H_2 oxidation was clearly related to the adlayers' structure.

Obtaining Pt monolayer catalysts for O_2 reduction is important for several reasons, including the possibility of reducing Pt loading, and of improving the activity of the catalysts. The initial results, obtained with a Pt monolayer deposited on Au using our new method of galvanic replacement of an adsorbed Cu monolayer, show the high activity of such surfaces.

Results

A thin-film rotating disk electrode (RDE) was used to determine catalytic activities and CO tolerance. Figure 1 shows the results of an accelerated test of CO tolerance of the PtRu₂₀ catalyst based on measuring the current at 0.05 V as a function of time for the oxidation of H_2 containing 1000 ppm CO at

60°C. For comparison, we include the results showing a smaller CO tolerance for two commercial catalysts, along with the results for PtRu₂₀ from the last review. A considerable improvement has been achieved; the CO tolerance of the PtRu₂₀ catalyst increased in this test from < 3 h to > 6 h.

Figure 2 shows the life test in MEA with an earlier version of the catalyst synthesized a year and a half ago. Clean H₂ and H₂ with 50 ppm CO and 4% air bleed were used as fuel. The losses after 1000 hours are 40 mV when the cell operates on clean H₂, and 60 mV with the H₂+50 ppm CO+4% air mixture. The cell was run with the latter fuel composition for a third of the total time. The test still is in progress. This result clearly shows that Pt submonolayers on Ru nanoparticles are stable during the fuel cell's operation and that this system represents a real catalyst. In addition to the high activity for H₂ oxidation and a weak CO bonding, the strong segregation of Pt and Ru is a key factor that determines this catalyst's stability. The data provide a powerful illustration of the possibility of nanoparticle surface modification by Pt monolayers as a method of obtaining low noble-metal loading of catalysts.

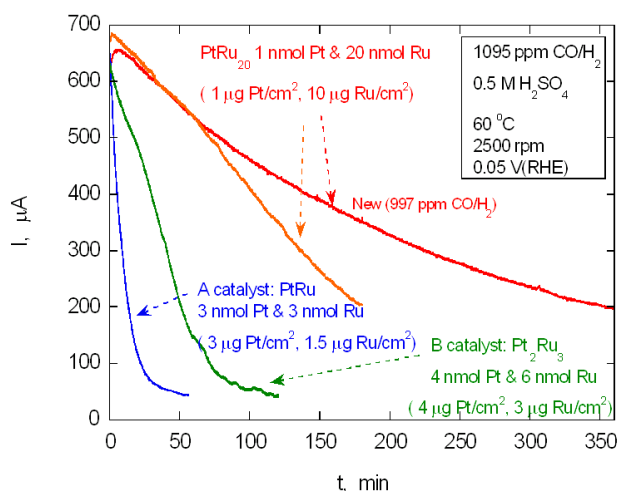


Figure 1. The CO tolerance of the improved PtRu₂₀ catalyst (top curve) compared with an earlier sample and two commercial catalysts. The current at 0.05 V is plotted as a function of time for the oxidation of H₂ containing 1000 ppm CO at 60°C; 2500 rpm. The catalyst loadings are given in the graph. RHE = reversible hydrogen electrode.

The ($\sqrt{19} \times \sqrt{19}$)13CO phase was determined for the first time on Pt(111) by *in situ* x-ray diffraction technique. We found that the $(2 \times 2) \leftrightarrow (\sqrt{19} \times \sqrt{19})$ phase transition occurs in several seconds. The oxidation of H₂ with 2% CO is inhibited by formation of the ordered CO (2 x 2) adlayer. Incomplete removal of CO disorders the phase, but the inhibition of H₂ oxidation remains unchanged.

To reduce the Ru loadings, RuNi and RuCo nanoparticles were deposited on XC-72 by wet impregnation, followed by spontaneous deposition of Pt. The activity of these catalysts for H₂ oxidation is somewhat lower than that of PtRu₂₀, while their CO tolerance is similar. Pt/Wpoly and Pt/W/C catalysts have a considerable activity for H₂ oxidation but poor CO tolerance.

Figure 3 displays rotating ring-disk electrode (RRDE) measurements of O₂ reduction on the Pt monolayer on an Au(111) surface, showing its very high activity ($E_{1/2} = 0.830$ V) and practically no H₂O₂ generation. Two Tafel slopes, usually observed with Pt electrodes, can be obtained from kinetic currents determined by the Koutecky-Levich plots. O₂ reduction on the Pt adlayer (9 μg Pt/cm²) on Au/C has $E_{1/2} = 0.820$ V. X-ray absorption

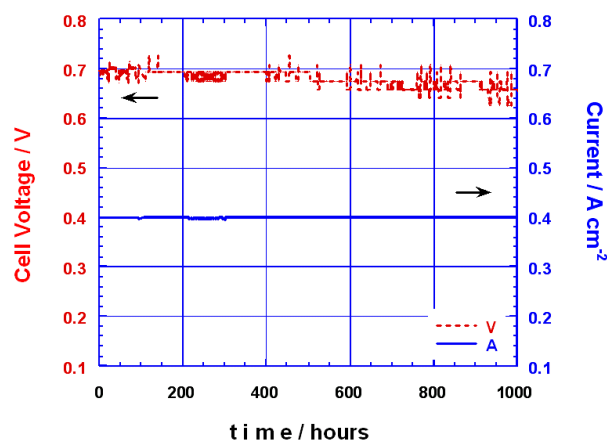


Figure 2. The long-term test in a cell conducted at LANL by F. Uribe and coworkers. Anode: 0.19 mg total metal/cm² (10%Ru, 1%Pt) 17 μg Pt/cm²; Cathode: 0.23 mg Pt (20% Pt/C, ETEK)/cm²; Electrode areas=50 cm²; T= 80°C; Pressures A/C = 30/30 psig. Total run time = 1000 hours at constant current (710 hours of operation with clean H₂ and 290 hours with H₂ + 50 ppm CO + 4 % air bleed).

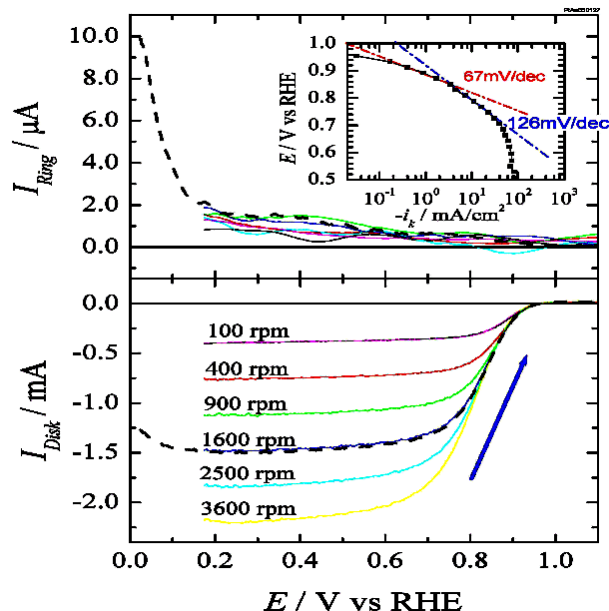


Figure 3. RRDE measurements of O_2 reduction on a $Pt_{1ML}/Au(111)$ surface. The insert shows the Tafel plot with kinetic currents obtained from the Koutecky-Levich plots.

spectroscopy measurements and voltammetry curves indicate that $PtOH$ formation on $Pt/Au/C$ and $Pt/Au(111)$ shifts to more positive potentials than those of Pt/C and $Pt(111)$ surfaces, respectively. This property may be very important for the function of these catalysts since $PtOH$ inhibits O_2 reduction. The long-term stability of the Pt/Au catalyst is questionable since this system is anti-segregated. These results, however, illustrate the important possibility that a Pt monolayer on metal nanoparticles can be an active catalyst for O_2 reduction.

Figure 4 is a histogram of the Pt -mass-specific activities of several bimetallic catalysts that we have tested so far. It shows that all the adlayer Pt deposits on Au nanoparticles have a higher Pt mass-specific activity than a standard 10% Pt/C catalyst. A mixed $Pt_{0.75}Pd_{0.25}$ catalyst performs the best.

Conclusions

The performance of the 1% Pt 10% Ru catalyst was considerably improved and a two-fold increase in CO tolerance achieved according to the

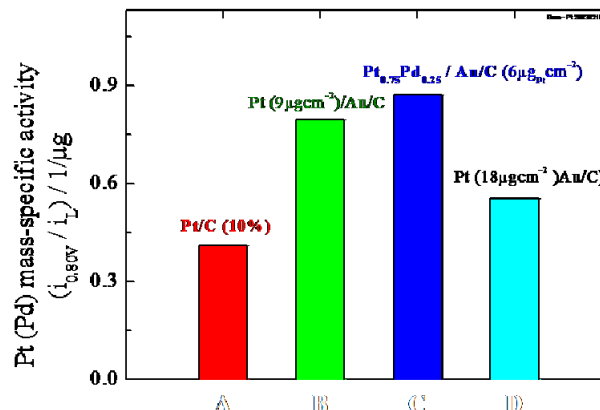


Figure 4. Histogram of the Pt -mass-specific activities of several bimetallic catalysts at $E=0.8$ V; 1600 rpm.

accelerated test with a rotating disk electrode. The long-term testing of the earlier version of the catalyst in MEA at LANL has reached 1000 hours in the oxidation of H_2 and $H_2 + 50$ ppm of CO and 4% of air with only a minor loss of performance. The test is still in progress. For Pt , the loading of the new catalyst is below the DOE's target ($150 \mu g/cm^2$) for precious metals for 2004. For Ru , it is at the present level of the state-of-the-art catalysts. As illustrated by the data for Pt on Au , Pt monolayers on metal nanoparticles can be active catalysts for O_2 reduction.

Publications

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3. J.X. Wang, S.R. Brankovic, Y. Zhu, J.C. Hanson, and R.R. Adzic, Kinetic Characterization of H_2 Anode Catalysts Made by Spontaneous Deposition of Pt on Ru Nanoparticles, *J. Electrochem. Soc.* in press.

4. K. Sasaki, Y. Mo, J.X. Wang, M. Balasubramanian, F. Uribe, J. McBreen, R.R. Adzic, Pt Submonolayers on Metal Nanoparticles - Novel Electrocatalysts for H₂ Oxidation and O₂ Reduction, *Electrochim. Acta*, in press.

Patents

1. Patent application submitted. The U.S. Patent Office serial number 09/812246.